

## Chapter 10

### Tight-Binding Method

(170)

Assume that in vicinity of each lattice point, the full periodic crystal Hamiltonian can be approximated by the Hamiltonian of a single atom located at the lattice point,  $H_{at}$

$$H_{at} \psi_n = E_n \psi_n$$

$n =$  ~~quantum number~~ level quantum number

$H_{at}$  will be an excellent approximation to  $H$  if  $H_{at} - H$  is very small over a distance from the lattice point up to at least the range of  $H_{at}$

- the range of  $H_{at}$  is the distance over which  $H_{at}$  is not small, measured from the lattice point

More generally

$$H = H_{at} + \Delta U(\vec{r}) \left. \vphantom{H} \right\} \begin{array}{l} \text{full} \\ \text{periodic} \\ \text{crystal} \\ \text{Hamiltonian} \end{array}$$

but  $\psi_n(\vec{r} - \vec{R})$ ,  $\vec{R} =$  Bravais lattice vector will be a ~~first~~ first approximation to the solution to the <sup>full</sup> crystal Hamiltonian equation

$$H \psi(\vec{r}) = \epsilon(\vec{k}) \psi(\vec{r})$$

The correction to  $H_{at}$  is  $\Delta U(\vec{r})$

(17)

If  $\psi_n(\vec{r})$  satisfies

$$H \psi_n(\vec{r}) = \varepsilon(\vec{k}) \psi_n(\vec{r})$$

then each  $\psi_n(\vec{r}) \rightarrow N$  levels,  $n = 1, \dots, N$

with wave function

$N =$  number of  
lattice sites

$$\psi_n(\vec{r} - \vec{R}) \text{ for all } \vec{R} \\ \text{in the lattice}$$

The total solution must be a linear combination of these wave functions (degenerate)

satisfying Bloch theorem

$$\psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r})$$

Suppose the following linear combination will work

$$\psi_{nh}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \psi_n(\vec{r} - \vec{R})$$

Show that this works:

$$\begin{aligned} \rightarrow \psi_{nh}(\vec{r} + \vec{R}) &= \sum_{\vec{R}'} e^{i\vec{k} \cdot \vec{R}'} \psi_n(\vec{r} + \vec{R} - \vec{R}') \\ &= e^{i\vec{k} \cdot \vec{R}} \sum_{\vec{R}'} e^{i\vec{k} \cdot (\vec{R}' - \vec{R})} \psi_n(\vec{r} + \vec{R} - \vec{R}') \end{aligned}$$

$$\rightarrow \psi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \sum_{\vec{r}'} e^{i\vec{k} \cdot (\vec{r}' - \vec{R})} \psi_n(\vec{r}' - \vec{R}) \quad (172)$$

$$= e^{i\vec{k} \cdot \vec{R}} \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} \psi_n(\vec{r} - \vec{R})$$

$$\psi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{n\vec{k}}(\vec{r})$$

satisfies Bloch theorem

There are  $N$  linear combinations of  $\psi_n(\vec{r} - \vec{R})$

They are:

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} \psi_n(\vec{r} - \vec{R})$$

- $\vec{k}$  takes on all possible values in the first Brillouin zone
- repetitions of course in other Brillouin zones at values  $\vec{k}' = \vec{k} - \vec{K}$

$$\vec{k} = \vec{k}_1, \vec{k}_2, \dots, \vec{k}_N$$

$$\vec{k} = \sum_{i=1}^3 \frac{m_i}{N_i} \vec{b}_i, \quad \vec{b}_i = \text{primitive reciprocal lattice vectors}$$

$$\vec{k} = \frac{m_1}{N_1} \vec{b}_1 + \frac{m_2}{N_2} \vec{b}_2 + \frac{m_3}{N_3} \vec{b}_3, \quad m_i \text{ are integers}$$

$$N = N_1 N_2 N_3$$

$$m_i = 1, \dots, N_i \text{ etc.}$$

The energy bands from the  $\psi_{n\vec{h}}(\vec{r})$  will just have energies

$$E_n(\vec{h}) = E_n$$

independent of  $\vec{h}$

This is not realistic.

$\Rightarrow$  must consider overlapping of  $\psi_n(\vec{r})$  and  $\Delta U(\vec{r})$  and find the more realistic solution

$$\psi(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi(\vec{r}-\vec{R})$$

$\phi(\vec{r})$  not necessarily an exact atomic stationary state wave-function

$\phi(\vec{r})$  to be determined

~~point~~ point is to find  $\phi(\vec{r})$  as an expansion in  $\psi_n(\vec{r})$

$$\Rightarrow \phi(\vec{r}) = \sum_n b_n \psi_n(\vec{r})$$

Since the  $\psi_n(\vec{r})$  are atomic wavefunctions, this method is sometimes referred to as the method of linear combination of atomic orbitals (LCAO)

$$\int [H\psi] \psi_m^*(\vec{r}) d\vec{r} = \varepsilon(\hbar) \int \psi \psi_m^* d\vec{r}$$

(174)

$$= \int [H_{\text{at}} + \Delta U(\vec{r})] \psi(\vec{r}) \psi_m^*(\vec{r}) d\vec{r}$$

$$= \int [H_{\text{at}} \psi(\vec{r})] \psi_m^*(\vec{r}) d\vec{r} + \int [\Delta U(\vec{r}) \psi(\vec{r})] \psi_m^*(\vec{r}) d\vec{r}$$

$$\varepsilon(\hbar) \int \psi(\vec{r}) \psi_m^*(\vec{r}) d\vec{r} = E_m \int \psi(\vec{r}) \psi_m^*(\vec{r}) d\vec{r} + \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi(\vec{r}) d\vec{r}$$

$$\Rightarrow \left( \varepsilon(\hbar) - E_m \right) \int \psi_m^*(\vec{r}) \psi(\vec{r}) d\vec{r} = \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi(\vec{r}) d\vec{r}$$

Using this equation we insert

$$\psi(\vec{r}) = \sum_{\vec{R}} e^{i\vec{h} \cdot \vec{R}} \phi(\vec{r} - \vec{R})$$

$$\psi(\vec{r}) = \sum_{\vec{R}} e^{i\vec{h} \cdot \vec{R}} \sum_n b_n \psi_n(\vec{r} - \vec{R})$$

$$(\mathcal{E}(\vec{r}) - E_m) \int \psi_m^*(\vec{r}) \left[ \sum_{\vec{R}} e^{i\vec{h} \cdot \vec{R}} \sum_n b_n \psi_n(\vec{r} - \vec{R}) \right] d\vec{r}$$

(175)

$$= \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \left[ \sum_{\vec{R}} e^{i\vec{h} \cdot \vec{R}} \sum_n b_n \psi_n(\vec{r} - \vec{R}) \right] d\vec{r}$$

Consider also that

$$\int \psi_m^*(\vec{r}) \psi_n(\vec{r}) d\vec{r} = \delta_{nm} \left. \vphantom{\int} \right\} \begin{array}{l} \text{orthonormality} \\ \text{of} \\ \text{atomic} \\ \text{wave functions} \end{array}$$

$$\Rightarrow (\mathcal{E}(\vec{r}) - E_m) \int \psi_m^*(\vec{r}) \sum_n b_n \psi_n(\vec{r}) d\vec{r}$$

$$+ \left[ (\mathcal{E}(\vec{r}) - E_m) \int \psi_m^*(\vec{r}) \sum_{\vec{R} \neq 0} e^{i\vec{h} \cdot \vec{R}} \sum_n b_n \psi_n(\vec{r} - \vec{R}) d\vec{r} \right] = \text{RHS}$$

$$\Rightarrow (\mathcal{E}(\vec{r}) - E_m) b_m + [\dots] = \text{RHS}$$

$$\Rightarrow (\mathcal{E}(\vec{r}) - E_m) b_m = - (\mathcal{E}(\vec{r}) - E_m) \sum_n \left( \sum_{\vec{R} \neq 0} \int \psi_m^*(\vec{r}) \psi_n(\vec{r} - \vec{R}) e^{i\vec{h} \cdot \vec{R}} d\vec{r} \right) b_n$$

$$+ \sum_n \left( \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi_n(\vec{r}) d\vec{r} \right) b_n$$

$$+ \sum_n \left( \sum_{\vec{R} \neq 0} \int \psi_m^*(\vec{r}) \Delta U(\vec{r}) \psi_n(\vec{r} - \vec{R}) e^{i\vec{h} \cdot \vec{R}} d\vec{r} \right) b_n$$

first term contains integrals of the form

(176)

$$\int d\vec{r} \psi_m^*(\vec{r}) \psi_n(\vec{r}-\vec{R}) \quad \left. \vphantom{\int} \right\} \begin{array}{l} \text{overlap} \\ \text{integral} \end{array}$$

assumption of well-localized atomic levels

$\Rightarrow$  overlap integral is small compared to unity

similarly for the 3<sup>rd</sup> term on RHS

$\Rightarrow$  small compared to unity

and for the reason that

$\Rightarrow$  we assume that the second term on the RHS is small because

"we expect the atomic wave functions to become small at distances large enough for the periodic potential to deviate appreciably from the atomic one."

$\Rightarrow (\mathcal{E}(\vec{k}) - E_m) b_m$  is always small

Ashcroft &  
Mermin,  
Solid State  
Physics,  
p. 180

This is possible if

$\epsilon(\vec{k}) - E_m$  is small whenever  $b_m$  is not small  
and if

$b_m$  is small whenever  $\epsilon(\vec{k}) - E_m$  is not small

$\Rightarrow \epsilon(\vec{k}) \approx E_m = E_0$  and  $(b_m \approx 0, \text{ unless } E_m \approx E_0)$

In other words,

$\epsilon(\vec{k})$  is close to an atomic level with  
not small  $b_m$

otherwise, the  $b_m$ 's are small

If  $b_m$ 's are small ~~the associated  $\psi_m(\vec{r})$ 's don't contribute~~

the associated  $\psi_m(\vec{r})$ 's don't contribute  
much to the wavefunction  
solution

Note that the  $b$ 's are  
actually  $b(\vec{k})$ 's  $\rightarrow$  there will be  $b_n(\vec{k})$ 's for each  
 $k$  in the Brillouin zone